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Catalytic hydrogenation of short chain carboxylic acids typical of model compound found in bio-oils

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ABSTRACT: Due to the complexity of bio-oil many studies have focused on model compounds which mimic components in bio-oil. In this paper, the hydrogenation of short chain (C₂-C₄) carboxylic acids in hexane using a Parr reactor and commercial Pt supported on Al₂O₃, SiO₂, carbon and graphite and prepared Pt and Pt-Re on TiO₂ catalysts was studied. With acetic acid, ethanol selectivity was found to be 80% (4%Pt-4%Re/TiO₂), 23% (4%Pt/TiO₂) and no ethanol was observed with the other catalysts at 200 °C, 40 bar, 0.3 g catalyst and 1000 min⁻¹. A Taguchi optimization approach was carried out from temperature 80-200 °C, pressure 10-40 bar, time 1-4 h, catalyst 0.1-0.4 g and stirring speed 400-1000 min⁻¹ using 4%Pt/TiO₂. The optimum conditions determined were 160 °C, 40 bar, 4 h, 0.4 g and 1000 min⁻¹ for ethanol production. 4%Pt/TiO₂ was

more selective towards esters while 4%Pt-Re/TiO₂ increased alcohols production with increasing Re (1-4%) loading.

1. INTRODUCTION

A large portion of liquid transportation fuels are obtained from petroleum reserves which are believed to have peaked and are now in decline. In addition, legislative and environmental challenges associated with petroleum based fuels¹ make bio-oil a renewable alternative to resolve these challenges. However, unprocessed bio-oil has limited use as fuel due to high viscosity, high acidity, chemical instability and complexity.^{2,3} Upgrading is therefore necessary to improve its fuel characteristics. Hydrodeoxygenation appears to be the preferred upgrading technique but has been faced with challenges of catalyst deactivation and uneconomical process costs among others.⁴ The complexity of bio-oil makes it difficult to understand the chemistry of the carboxylic acid components during upgrading; hence, model compound studies have been adopted and reported in the literature for a range of classes of compounds found in bio-oil such as ketones, aromatics and aldehydes. However, model studies regarding carboxylic acids mostly consider long chain acids.

Hydrogenation of carboxylic acids to produce alcohols and other platform chemicals is a significant synthetic transformation for biomass utilization and chemical industries.⁵ This reaction involves the use of molecular hydrogen as a reducing agent and offers 100% atom efficiency.⁶ Nevertheless, carboxylic acids are difficult to hydrogenate because they are thermodynamically and kinetically stable which results from the low electrophilicity of the carbonyl carbon.^{7,8} Additional difficulty results from the low polarizability of the carbonyl group present in carboxylic acids which makes them less reactive towards reduction. In contrast to the hydrogenation of amides, esters and other carbonyl compounds which is a straightforward and effective synthetic method to generate alcohols and other fine chemicals, hydrogenation of carboxylic acids has

gained less attention and lags behind.^{6,9,10} Due to the complexities associated with carboxylic acid towards hydrogenation, the formulation of an efficient and deactivation resistant catalyst is sought.

Selective hydrogenation of carboxylic acids into alcohols and other bulk platform chemicals offers great potential in the utilization of bio-oil model compounds. However, most of these processes require harsh operating conditions which results in the degradation of reactants and formation of side products.^{5,11} Therefore, catalyst performance to improve the process in terms of selectivity and economic efficiency is desirable. Ullrich and Breit¹² reported that the hydrogenation of long chain carboxylic acids proceeds via hydrogenation-dehydration-hydrogenation reaction route to generate alcohols and alkanes as primary products. In a similar study, Manyar et al.¹³ have reported the hydrogenation of fatty acids using titania supported Pt catalysts to produce alcohols and alkanes at relatively mild conditions. Furthermore, Takeda et al.¹⁴ reported the selective hydrogenation of higher fatty acids (C₆-C₁₈) into alcohols using ReOx–Pd/SiO₂. This study aims to maximise the alcohol production from the carboxylic acid components of bio-oil because they are relevant fuel products; therefore, a catalyst that maximises alcohol production from the hydrogenation of short chain carboxylic acids was formulated, prepared and screened against commercial counterparts such as Pt/C, Pt/Al₂O₃ and Pt/SiO₂ commonly used in upgrading bio-oil. In the same vein, the influence of operational conditions on alcohol yield was also optimised based on the Taguchi approach. Consequently, the effect of impregnating rhenium (Re) onto the Pt/TiO₂ catalyst as a promoter, and its role in suppressing esterification reactions while maximising alcohol production was also investigated. As a consequence, a comparative study between 4% Pt/TiO₂ and bi-metallic 4% Pt-4% Re/TiO₂ was carried out and their performance reported for the hydrogenation of acetic, propanoic and butanoic acids typical short chain carboxylic acids found in bio-oils.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. 4% Pt/TiO₂ and 4% Pt–4% Re/TiO₂ catalysts were prepared by incipient wetness impregnation method from titanium dioxide [TiO₂ (P90)], platinum (IV) nitrate [Pt(NO₃)₄ (15% w/w)] and perrhenic acid [HReO₄ (75-80 wt%, aqueous)]. About 3 g of platinum (IV) nitrate was added dropwise to approximately 10 g of titania (P90) to formulate 10 g of 4% Pt/TiO₂. Similarly, for the preparation of 4% Pt–4% Re/TiO₂, 2.67 g platinum (IV) nitrate and 0.75 g of perrhenic acid were added to 9.2 g of titania (TiO₂ P90). Consequently, 100 ml of methanol was added to the mixture and stirred overnight using a magnetic stirrer to achieve a homogenous mixture. Furthermore, the mixture was dried under air and the resulting solid residue was oven dried for 3 hours at 80 °C. Thereafter, the solid was ground to powder form using a pestle and mortar, and calcined at 500 °C under air flow for 4 hours. The prepared catalyst was evaluated against the following commercial catalysts Pt/C (Sigma Aldrich), Pt/graphite, Pt/SiO₂ and Pt/Al₂O₃ (Johnson Matthey).

2.2. Catalyst Characterization. Prepared catalysts were characterized using a range of analytical techniques. The X-Ray diffraction (XRD) patterns for the different crystal phases were obtained using a D2 Bruker diffractometer and Cu K α (1.54) radiation. The data were recorded using a step size of 0.37 in the 2 θ ranges of 10-100 °C. The XRD patterns obtained were identified by matching them against XRD patterns from the literature.

The elemental mapping was obtained using a SEM Hitachi TM3030 Plus equipped with a Bruker Quantax 70 energy dispersive X-ray spectroscopy (EDX). The powdered catalyst samples were placed on a microscope stub with carbon strip, then analysed using the SEM Hitachi TM3030 equipment under an accelerated voltage of 15 kV. The resulting images are generated by signals

obtained from back scattered electrons (BSE) by manual focusing on a selected region of about 30 μm width at 2500 \times magnification.

The Brunauer – Emmett – Teller (BET) equation was used to determine the catalyst surface area and the Barrett-Joyner-Halenda (BJH) model was used to estimate pore size, using Micromeritics Analytical Instrument ASAP 2010 at 77 K in accordance with adsorption and desorption of nitrogen on a given amount of the catalyst.

A Quantachrom ChemBet Pulsar equipped with a thermal conductivity detector (TCD) was used for temperature programmed reduction (TPR) measurements of the catalysts. About 20 mg of catalyst was loaded into a quartz U-tube reactor and plugged with quartz wool. The sample was pre-treated under 10% O_2/He at 300 $^\circ\text{C}$ for 60 min at a total flow of 40 $\text{cm}^3 \text{min}^{-1}$ to eliminate any volatile component. Subsequently, the H_2 -TPR was initiated by decreasing the temperature to -50 $^\circ\text{C}$, whereupon 5% H_2/Ar was introduced and the temperature increased from -50 $^\circ\text{C}$ to 800 $^\circ\text{C}$ at 5 $^\circ\text{C min}^{-1}$.

2.3. Experimental Procedure. A 100 ml stirred batch reactor (Parr Instruments Company) was used to carry out catalytic activity studies in hexane solvent. The reactor is equipped with a mechanical stirrer, a thermocouple, a pressure gauge, a controller system for temperature and stirring rate. It also is fitted with a rupture disk, inlet and outlet gas ports and modified liquid sampling port. The reactor has a maximum operating capacity of 350 $^\circ\text{C}$ and 180 bar. For reactions that involve the use of titania supported catalysts, the catalysts were reduced in-situ prior to reaction at 20 bar H_2 , 200 $^\circ\text{C}$ and 1000 min^{-1} for 65 min. For each experiment, a desired amount of reactant solution was charged into the reactor with a required amount of powdered solid catalyst. The reactor was sealed and pressurized to 10 bar of hydrogen gas. The reactor was purged three times and then subsequently, pressurised to 60 bar hydrogen to monitor and ensure a leak-proof

system. Thereafter, hydrogen gas was released through the gas outlet port leaving the desired amount of hydrogen gas for the reaction which was ≤ 40 bar. The gas lines and gas bottle regulator were closed off prior to heating the reactor. The reactor content was mixed using a stirring speed of 1000 min^{-1} and heating was commenced afterwards to initiate the reaction start time. All experiments were repeated and reproduced within an error of less than 1.5%.

2.4. Optimization of Process Factors. Different approaches of Design of experiment (DOE) have been widely reported in providing a predictive knowledge for complex and multi-variable processes with a few trial runs such as hydrogenation of model compounds.^{15,16} The Taguchi method was used to optimise the reaction factors and their contribution towards maximising the conversion of acetic acid and yield of ethanol in the hydrogenation of acetic acid over a 4%Pt/TiO₂ catalyst.¹⁷ The reaction factors include reaction temperature, initial hydrogen pressure, catalyst loading, reaction time and stirring speed. In the literature, at temperatures greater than 240 °C the products of acetic acid hydrogenation were methane, ethane and carbon dioxide.^{18–20} In this study, preliminary experiments was carried out to determine the temperature that supports the formation of liquid products such as ethylacetate and ethanol. It was found that at 200 °C and 240 °C the acetic conversion were 95% and 96% while the amount of ethanol produced was higher at 200 °C than 240 °C. Therefore, 200 °C was selected as the maximum temperature. Also, a preliminary study on the effect of stirring speed on acetic conversion showed that external mass transfer effect was eliminated at 1000 min^{-1} as conversion remain plateaued from 1000 to 1400 min^{-1} ; hence, 1000 min^{-1} was selected as the maximum stirring speed (Figure S1). Table 1 shows the range of factors considered for the optimization. An orthogonal array of sixteen experimental runs (L16) that describes five reaction factors and four different levels was designed to simultaneously study the effect of the process variables with respect to mean response. Considering the three types of

S/N ratios such as smaller-the-better, larger-the-better and nominal the best as investigated by Ross,¹⁶ the objective, herein, is to maximise the conversion of acetic acid and yield of ethanol; hence, the larger-the-better S/N ratio function is used as shown in Eq. (1).

$$\left(\frac{S}{N}\right) = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right)$$

where n = number of experimental repetitions, y_i = the conversion of the i th experiment and y_i^2 mean square of measure response value. The analysis of variance (ANOVA) and mean of response were employed to evaluate the influence of the reaction factors and their optimum values.

Table 1. Reaction factors and their levels.

Factors	Levels			
	1	2	3	4
Temperature (°C)	80	120	160	200
Initial Pressure (bar)	10	20	30	40
Catalyst Loading (g)	0.1	0.2	0.3	0.4
Stirring Speed (min ⁻¹)	400	600	800	1000
Reaction Time (h)	1	2	3	4

2.5. Product Analysis. The liquid products were analysed using a Trace GC Ultra equipped with a flame ionization detector (FID) and a ZB-Wax capillary column (30 m × 0.25 mm × 0.25 μm). The amount of gas phase products was insignificant and related to the unaccounted mass from the mass balance of product mixture. The GC equipment was operated under a constant pressure of 150 kPa with helium as the carrier gas. The injector and detector temperatures were both set at 250

°C. The oven temperature was programmed as thus: held at 40 °C for 5 minutes and then subsequently ramped to 215 °C at 20 °C min⁻¹, further ramped to 220 °C at 5 °C min⁻¹ and held at 220 °C for 5 minutes. 1 µL of sample was injected into the column by using a split ratio of 181:1 for each analysis. The following equations were used to quantify the carboxylic acid conversion, product selectivity and alcohol yield.

$$\text{Conversion (\%)} = \frac{(\text{Initial moles of acid} - \text{Final moles of acid})}{\text{Initial moles of acid}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{Moles of desired product}}{\text{Total moles of products formed}} \times 100$$

$$\text{Alcohol Yield (\%)} = \text{Conversion (starting material)} \times \text{Selectivity (desired product)} \times 100$$

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. Figure 1 shows the H₂-TPR profiles of 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂ catalysts. 4%Pt/TiO₂ showed two distinct H₂ consumption peaks in the range of 6 – 140 °C and 430 – 650 °C, and centroids at 42 °C and 560 °C, respectively. The low temperature peak corresponds to reduction of Pt⁴⁺ (PtO₂) impregnated into the 4% Pt/TiO₂ to Pt⁰ in the presence of hydrogen gas. It is worth noting that the reduction of bulk oxygen of TiO₂ occurs at temperatures higher than 600 °C.^{21–23} Thus, the broad peak between 300 °C and 600 °C can be ascribed to partial or complete reduction of the oxygen on the TiO₂,²² which means TiO₂ reduction was very tough. Pritchard et al.²⁴ performed X-ray Photoelectron Spectroscopy (XPS) on Pt/TiO₂ and Pt-Re/TiO₂ catalysts which are the same as those used in this study, and found that the addition of Re to Pt/TiO₂ slightly increased the binding energy from 71 to 71.7 eV, which suggest a good contact between

Re and Pt and a strong interaction with the support. In addition, PtO_2 is highly dispersed inside the pores of TiO_2 which is confirmed by the absence of Pt peaks in the XRD profile and EDX mapping of 4%Pt/ TiO_2 (Figure S2 and S3 respectively). For the 4%Pt - 4%Re/ TiO_2 catalyst, TPR showed three peaks in different ranges of reduction temperature. The H_2 consumption peaks show that Pt^{4+} and Re^{7+} are reduced to Pt^0 and Re^0 , which corresponds to the peaks at 20 – 160 °C and 170 – 260 °C, respectively. It is evident that the addition of 4% Re resulted in a change of the peak shapes and a slight drift in the reduction centroids of the Pt and TiO_2 reduction peaks towards the higher temperatures, which in turn increases the intensity of the Pt reduction peak.^{25,26} In this study, a temperature of 200 °C was used for H_2 reduction of 4%Pt/ TiO_2 and 4%Pt-4%Re/ TiO_2 catalysts.

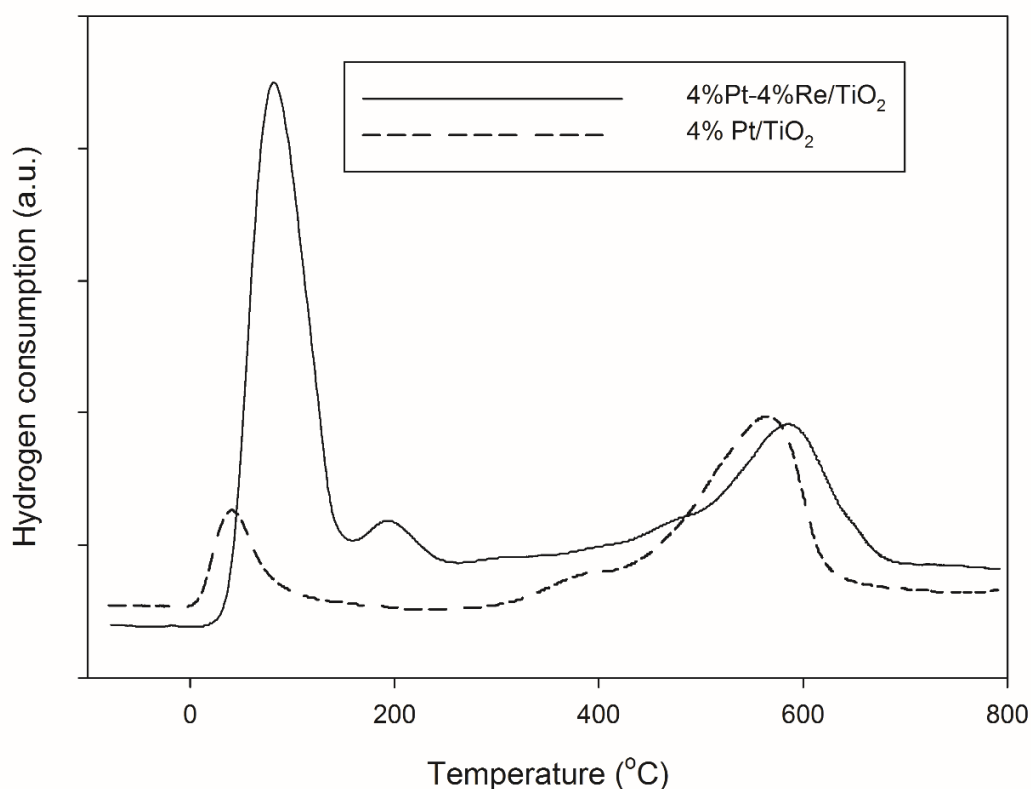


Figure 1. TPR profiles of 4% Pt/ TiO_2 and 4% Pt - 4% Re/ TiO_2 catalysts.

3.2. Screening of commercial and prepared catalysts. The effects of different Pt based catalysts supported on SiO₂, Al₂O₃, carbon, graphite and TiO₂ was carried out under identical reaction conditions of 40 bar, 200 °C, 4 hours, 0.3 g catalyst and 1000 min⁻¹, with the resulting conversion and selectivities shown in Figure 2. During liquid phase hydrogenation, the rate of reaction can be affected by solvent adsorption on the catalyst support and active metal which could influence the adsorption equilibria of reactants and hydrogen solubility.^{27–29} For example, alcohol solvents such as methanol exhibit a strong polarity and can react with the acid reagent shifting the reaction equilibrium towards production of methyl esters during hydrogenation of carboxylic acids lowering the selectivity to the desired hydrogenation products.^{30,31} Several publications have reported the use of alkane solvents for the study of hydrogenation of bio-oil model compounds.^{29,32} Pritchard et al.⁵ studied the hydrogenation of esters to alcohols and reported that hexane was the optimal solvent from solvent screening. Herein, the use of hexane as a solvent is reported.

As shown in Figure 2, Pt/SiO₂ and Pt/Al₂O₃ showed the lowest conversion with little or no formation of the desired product (ethanol and ethylacetate). Decarboxylation and decarbonylation reactions mainly dominated on Pt/SiO₂ and Pt/Al₂O₃ with carbon loss to produce CO which was further hydrogenated to produce CH₄.³³ The gaseous products formed were negligible which corresponds to the low conversion and mass balance obtained from the analysis (< 1.5% for gases). Similarly, recent studies reported a low conversion for Pt/SiO₂ and Pt/Al₂O₃, and high selectivity towards CO and CH₄ with additional traces of ethanol, ethylacetate and ethane for Pt/Al₂O₃ for hydrogenation of acetic acid in water.^{18,34} Furthermore, the production of CO and CH₄ over Pt/SiO₂ reported for aqueous phase study is linked with this study.^{33,35} Elsewhere, Manyar et al.¹³ studied the hydrogenation of stearic acid and found that the conversion over Pt/SiO₂ and Pt/Al₂O₃ was ≤ 2% even after 24 h.

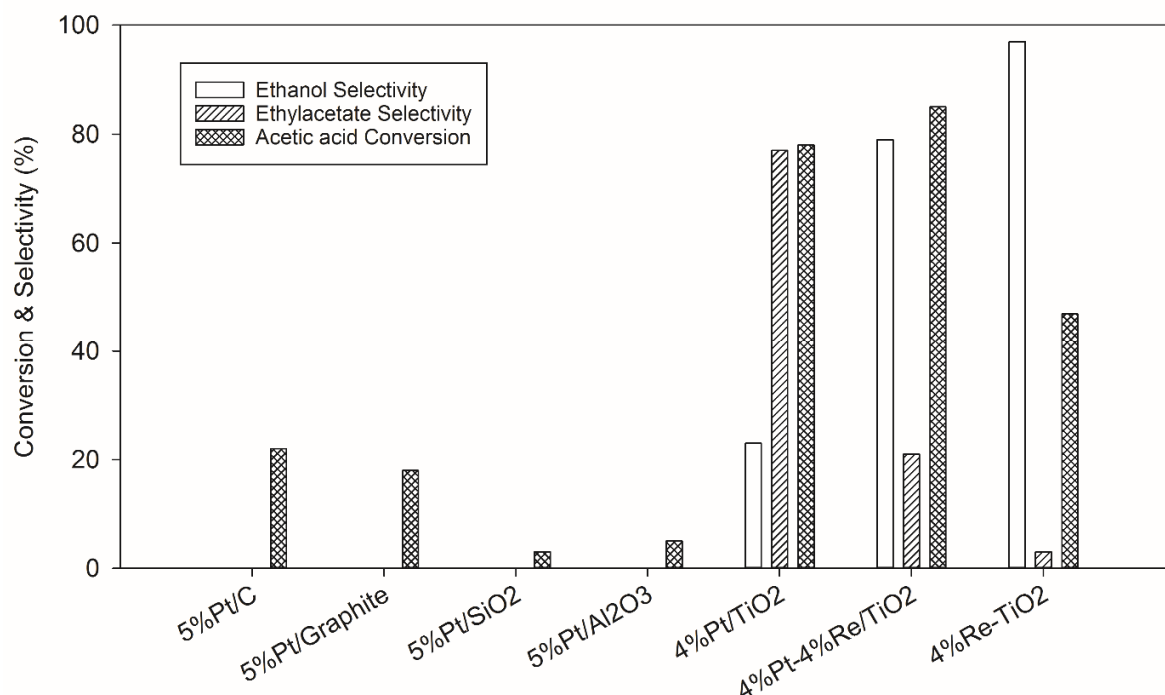


Figure 2. Conversion and selectivity of different catalysts (Reaction conditions: catalyst 0.3 g, temperature 200 °C, initial concentration 0.521 M, reaction time 4 h, pressure 40 bar; Standard deviation: Pt/C, ± 0.08 ; Pt/graphite, ± 0.002 ; Pt/SiO₂, ± 0.0008 ; Pt/Al₂O₃, ± 0.006 ; Pt/TiO₂, ± 0.001 ; Pt-Re/TiO₂, ± 0.008).

Pt/C and Pt/graphite showed a conversion of 22% and 18%, respectively, but no liquid product was formed. However, gaseous products such as methane, CO₂ and ethane have been reported for hydrogenation of acetic acid over Pt/C in the range of 150-300 °C.¹⁸ Hence, the observed conversion could be attributed to the formation of these gaseous products. In spite of the improved conversion compared to Pt/SiO₂ and Pt/Al₂O₃, there was no observed formation of desired liquid products which confirms the absence of acidic properties on the carbon and graphite supports, and the limitation of platinum metal sites as the only platform for H₂ activation and acetic acid

adsorption.^{36–38} It was also observed that the catalyst activity cannot be attributed to the high surface area possessed by Pt/C (Table S1). Wan et al.¹⁸ studied the aqueous phase hydrogenation of acetic acid over Pt/C and observed the major products to be CH₄ and CO₂ with traces of C₂H₆ which explains the observation in Figure 2 for Pt/C and Pt/graphite.

He and Wang³³ reported that Pt/TiO₂ favours ethane and acetaldehyde formation while Pt/C favours ethanol using a fixed reactor despite the strength of Pt and support interaction being approximately the same for both carbon and TiO₂. However, in this study, it can be observed that the use of TiO₂ as a support for Pt is more effective for the conversion of acetic acid and the production of ethanol and ethylacetate when compared to other supports such as carbon, alumina and silica (Figure 2). This has been linked to the strength of the acid sites on TiO₂ and its interaction with the impregnated Pt/Pt-Re species.²⁴ As a consequence, the adsorption of carbonyl species was primarily through interaction with the Tiⁿ⁺ cations (Lewis acid sites) and/or oxygen vacancies created in the reducible oxide after the reduction at 200 °C, these sites can activate the acid carbonyl group for hydrogenation. With Pt providing dissociated hydrogen and the adsorption sites on TiO₂ activating the carbonyl group, Pt/TiO₂ promotes the hydrogenation reaction to the formation of ethanol.^{2,39} In contrast, the absence of oxygen vacancies and the neutrality of the Pt/C and Pt/graphite could alter the adsorption of acetic acid favouring decomposition reactions over hydrogenation with activation of both hydrogen and the acids occurring on the Pt sites.^{37,38}

Conversely, the formulated 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂ catalysts showed significant conversions of 78% and 83%, respectively, in addition to the formation of the desired products (see Figure 2). However, while 4%Pt/TiO₂ is more selective towards ethylacetate, the selectivity towards ethanol was more favoured by 4%Pt-4%Re/TiO₂. It is worth noting that no reaction occurred over titania without Pt or Re metal impregnated. The impregnation of Re only

(4%Re/TiO₂) strongly favoured the selectivity to ethanol compared to ethylacetate. It is clear, therefore, that the presence of Re magnified the route to ethanol production while suppressing that leading to ethylacetate formation. This is confirmed from the results of the use of Pt, Re and Pt-Re shown in Figure 2. Although, the selectivity to ethanol is high with 4%Re/TiO₂, the conversion of acetic acid is low at 47% compared to 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂. Hence, addition of Re influences the catalyst activity and performance. The opposite trend in product selectivity over 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂ catalysts can be distinguished by the presence of highly oxophilic Re centres present in 4%Pt-4%Re/TiO₂ which makes them highly potent to C=O reduction of the acetic acid.⁵ When compared to the observation with 4%Pt/TiO₂, the synergistic effect of Pt and Re showed that Pt facilitates the hydrogenation activity of the catalyst likely through dissociation of H₂ while Re acts as a promoter, activating the C=O group. However, for stearic acid¹³ it has been reported that the addition of Re to Pt/TiO₂ enhanced the hydrogenation activity but reduced alcohol selectivity resulting in more alkane products. In the same study, it was observed that further increase in the Re loading to 4wt% enhanced the reaction rate but did not correlate with alcohol selectivity.

3.3. Optimization of Process Factors. The effect of reaction factors on the conversion of acetic acid and yield of ethanol over 4%Pt/TiO₂ was optimised and their relative contribution quantified. An orthogonal array of sixteen (16) experiments and the corresponding S/N ratios obtained are shown in Table 2. For each factor at a particular level, the total S/N ratio was calculated by summing the individual S/N ratios for the respective experiments. For example, the total S/N ratio for H₂ pressure at level 3 was obtained by adding the individual S/N ratio for experiment numbers 3, 7, 11, 15 (Table 2). The effect of reaction factors with respect to each level is graphically presented in Figure 3. The profile depicts that temperature reached its maximum at 200 °C and has

a profound effect with respect to the conversion of acetic acid. It can be observed that the total S/N ratios for each factor increased with each increase in level, thereby attaining the maximum at level 4. Even though C-O bond cleavage is catalytically driven and possesses high activation energy, it is evident that higher temperatures enhance the hydrogenolysis of C-O bonds towards aldehyde formation as an intermediate species, followed by the subsequent formation of ethanol and ethylacetate.

Table 2. Experimental design for L16 array and corresponding S/N ratio for reactions over Pt/TiO₂.

Experiment No.	A Temp. (°C)	B Pressure (bar)	C Time (h)	D Stirring (min ⁻¹)	E Catalyst (g)	Acetic acid Conversion (%)	S/N Conversion	Ethanol Yield (%)	S/N Yield
1	80	10	1	400	0.1	0.30	-10.46	0.05	-25.35
2	80	20	2	600	0.2	1.37	2.73	0.41	-7.72
3	80	30	3	800	0.3	3.79	11.57	2.08	6.38
4	80	40	4	1000	0.4	7.50	17.50	6.00	15.56
5	120	10	2	1000	0.3	29.11	29.28	16.01	24.09
6	120	20	1	800	0.4	17.61	24.92	13.91	22.87
7	120	30	4	600	0.1	36.45	31.23	25.52	28.14
8	120	40	3	400	0.2	35.14	30.91	29.86	29.50
9	160	10	3	600	0.4	65.07	36.27	33.19	30.42
10	160	20	4	400	0.3	70.68	36.99	37.46	31.47
11	160	30	1	1000	0.2	50.00	33.98	32.50	30.24
12	160	40	2	800	0.1	52.26	34.36	31.88	30.07
13	200	10	4	800	0.2	83.44	38.43	25.03	27.97
14	200	20	3	1000	0.1	81.95	38.27	28.68	29.15

15	200	30	2	400	0.4	79.30	37.99	38.06	31.61
16	200	40	1	600	0.3	68.19	36.67	13.64	22.69

The total S/N ratio of factor B increased linearly with pressure and reached an optimum at 40 bar. At prevailing conditions, the extent of hydrogen solubility in the reaction mixture improves hydrogen adsorption on the catalyst surface which in turn promotes hydrogen spill over to react with the adsorbed carbonyl species.⁴⁰

It was also observed that increased reaction time strongly favours conversion of acetic acid. Subsequently, the S/N ratio increased with reaction time which validates the maximum conversion achieved at a reaction time of 4 h, thus confirming the optimal reaction time to be level 4. The longer time required to achieve maximum conversion is associated with the difficulty in polarizing the carbonyl group of acetic acid and resistance to hydrogenation.⁵ The S/N ratio for factor D increases with stirring speed and attained maximum at level 4 which represents the highest level. From Figure 3, the increase in S/N ratio for stirring speed from level 2 to 4 was less significant which suggests that the extent of external mass transfer limitation is negligible. This observation conforms to findings from mass transfer investigations (Figure S1) which suggested that a stirring speed of 1000 min⁻¹ is sufficient to overcome limitations due to external mass transfer. The effect of Factor E on S/N ratio revealed that increased catalyst loading increased the conversion of acetic acid. The improved activity of the catalyst upon increase in loading in the reactor is attributed to the increase in the number of active sites which provides an efficient platform for adsorption of carbonyl carbon and hydrogen attack as activated on platinum. Based on the results obtained in Figure 3 and Table 3, the optimum reaction factors can be reported as thus: A₄, B₄, C₄, D₄, E₄ i.e., temperature 200 °C, initial hydrogen pressure 40 bar, reaction time 4 h, catalyst loading 0.4 g and stirring speed 1000 min⁻¹ respectively. To validate the optimization results, it is essential to carry

out a confirmation experiment using the optimum reaction factors from the Taguchi method, considering the fact that the optimum conditions did not form a set of experiments in the orthogonal array. The confirmation experiment was performed in duplicate (Table 3) and revealed that the conversion of acetic acid and corresponding S/N ratio was higher than the highest S/N ratio obtained in Experiment 13 of Table 2, thus confirming the applicability of the Taguchi method for optimizing the conversion of acetic acid using 4% Pt/TiO₂.

Table 3. Confirmation experiment under optimised conditions for conversion of acetic acid.

Experiment	Levels					Conversion (%)	S/N ratio
	A	B	C	D	E		
Exp. No. 13	4	1	4	3	2	83.44	38.43
Confirmation Exp.	4	4	4	4	4	94	39.46

In order to examine the contributory effect of each reaction factor with respect to conversion of acetic acid, ANOVA was carried out. Table 4 presents the ANOVA result where the contribution of each factor was estimated by comparison of individual mean variance (V). Based on the mean variances obtained, temperature exerted the highest impact on acetic acid conversion while stirring speed was the least influential controllable factor. However, the variance provides only qualitative information in estimating the most significant parameter.^{41,42} The percentage contribution of each controllable factor based on the ANOVA results can be summarized as thus: Temperature > reaction time > initial H₂ pressure > catalyst loading > stirring speed.

Table 4. Analysis of variance (ANOVA) for conversion of acetic acid.

Parameter	DOF	Sum Squares	of Variance	% Contribution
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Temperature	3	2646.49	882.16	84.70
Pressure	3	103.06	34.35	3.30
Stirrer Speed	3	70.54	23.51	2.30
Reaction time	3	219.74	73.25	7.00
Catalyst Weight	3	83.43	27.81	2.70
Error	1	0.00	0.000	
Total	16	3123.25		100

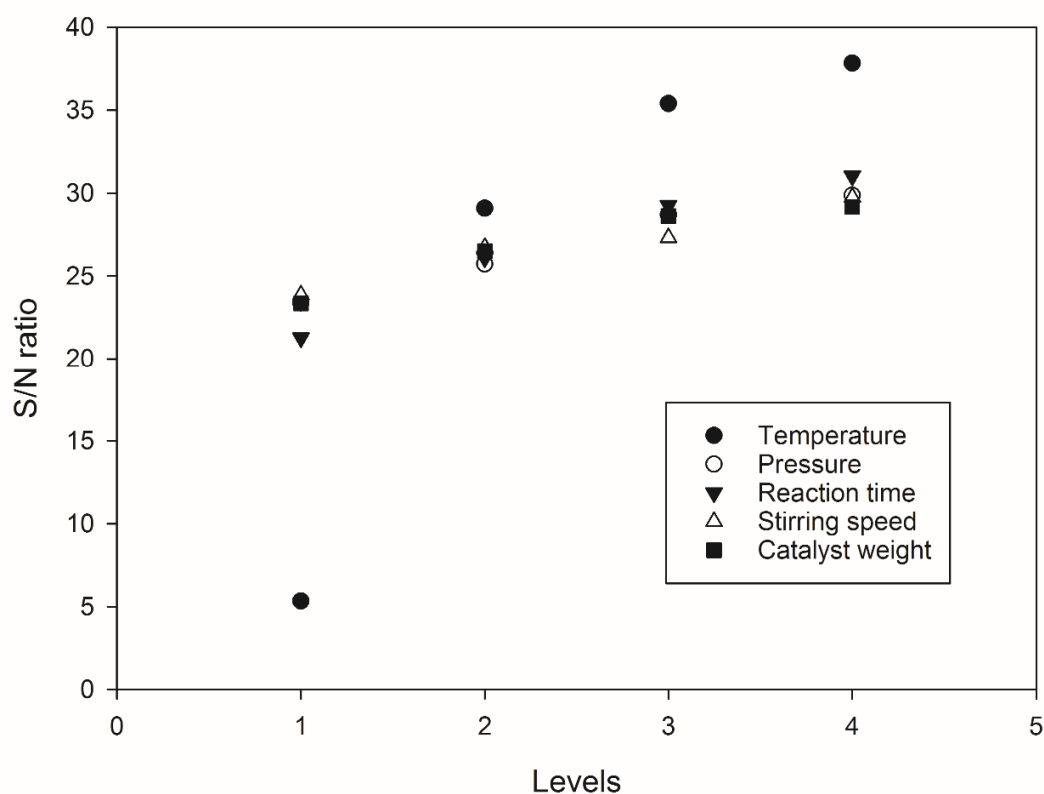


Figure 3. Effect of process factors at each level for conversion of acetic acid.

In order to maximise the yield of ethanol, the S/N ratio was calculated by considering the larger the better function (equation 1). The mean ethanol yield was calculated as shown in Table 2. As seen in Figure 4, the maximum S/N ratio for each factor was attained at level 4 with the exception

of temperature at level 3 (160 °C). Unlike the acetic acid conversion in which 200 °C (level 4) was the optimum, for ethanol production the temperature dropped to 160 °C which means beyond 160 °C there is a side reaction that favours ethyl acetate formation. It is worth noting that high pressure and high catalyst weight favours the selective hydrogenation of acetic acid to ethanol. Table 6 shows the confirmatory test experiment [160 °C (level 3), 40 bar (level 4), 4 h (level 4), 0.4 g (level 4) and 1000 min⁻¹ (level 4)]. This is compared to the highest ethanol yield reported in Table 2 which corresponds to experiment 15 as shown in Table 6. It is clear the ethanol yield and the S/N ratio at the achieved optimised condition is marginally higher than the best found in Table 2 (experiment 15). Table 5 shows the ANOVA analysis result for the yield of ethanol. Similar to the conversion of acetic acid, the ANOVA results with respect to ethanol yield is summarized as follows Temperature > reaction time > initial H₂ pressure > catalyst loading > stirring speed. This ranking order is consistent with that of the acetic acid conversion.

Table 5. Analysis of variance (ANOVA) for yield of ethanol.

Parameter	DOF	Sum of Squares	Variance	% Contribution
Temperature	3	2916.47	972.16	73.90
Pressure	3	278.58	92.86	7.10
Stirrer Speed	3	152.01	50.67	3.90
Reaction time	3	409.74	136.58	10.40
Catalyst Weight	3	187.81	62.60	4.80
Error	1	0.00	0.00	0.00
Total	16	10631.34	1314.87	100

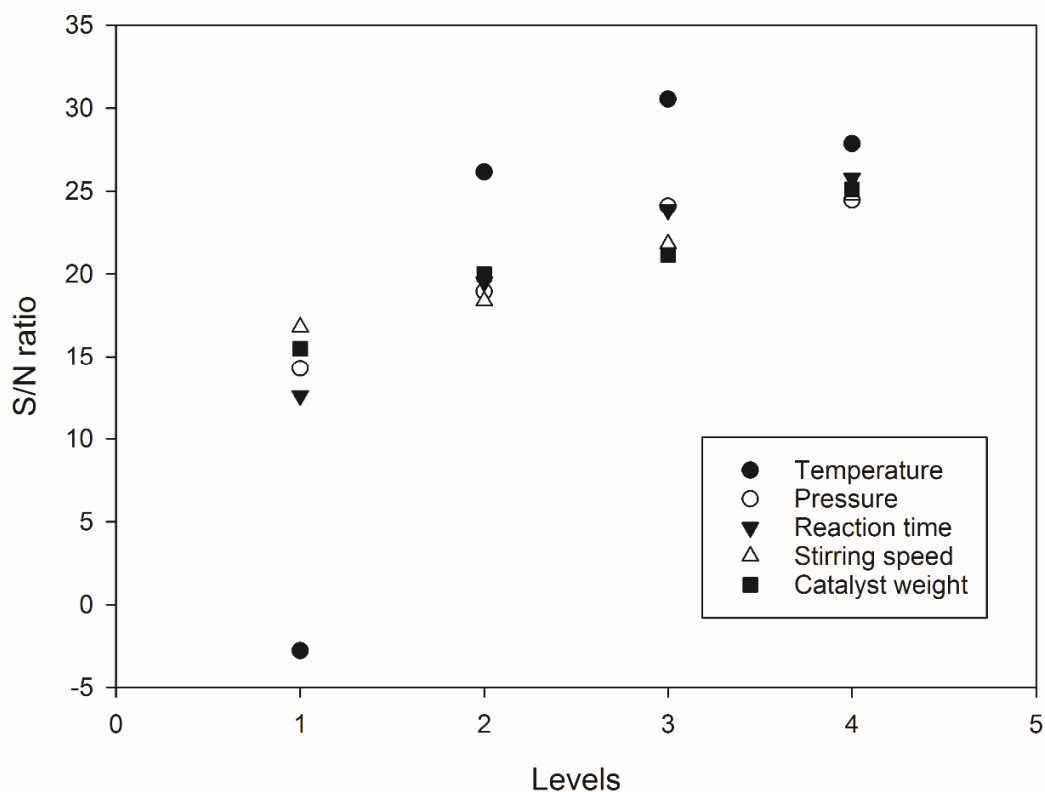


Figure 4. Effect of process factors at each level for yield of ethanol.

Table 6. Confirmation experiment under optimised conditions for yield of ethanol.

Experiment	Levels					Yield (%)	S/N ratio
	A	B	C	D	E		
Exp. No. 15	4	3	2	1	4	38.06	31.61
Confirmation Exp.	3	4	4	4	4	38.92	31.80

3.4. Effect of temperature on the Hydrogenation of C₂-C₄ carboxylic acids over 4% Pt/TiO₂ and 4% Pt4% Re/TiO₂. The effect of temperature in the range of 145-200 °C was investigated in terms of catalyst activity and product selectivity for the hydrogenation of acetic, propanoic and

butanoic acids over 4%Pt/TiO₂ and 4%Pt-4% Re/TiO₂. Table 7 shows the respective conversions of acetic, propanoic and butanoic acids and their selectivity towards alcohol and ester. It was observed that the production of liquid products was found to be $\geq 98\%$ which were mainly alcohols and esters corresponding to each acid. Typical gaseous products found were trace amounts of CO, CO₂ and C₁ - C₄ alkanes. It is clear that the conversion of the short chain carboxylic acids and their respective ester selectivity increased as the reaction temperature increased for the 4% Pt/TiO₂ catalyst. Under the same reaction temperature, the conversion of the carboxylic acid decreased as the carbon number increased from C₂ to C₄ while the selectivity of their respective alcohols increased as the carbon number within the carboxylic acid increased (Table 7). The observed conversion trend can be ascribed to the decreased volatility, increased boiling point and increased molecular size with increased carbon number in the carbonyl chain, which in turn decreases the diffusion of reactants into the catalyst particles.^{43,44} Conversely, alcohol selectivity increases with increasing carbon number of the corresponding carboxylic acid and decreasing polarity of the carbonyl (C=O) group (Table 7, the selective of the respective alcohols as a function reaction temperature with respect to 4%Pt/TiO₂). It can also be observed in Table 7 that the alcohol selectivity decreased as reaction temperature increased for 4%Pt/TiO₂ catalyst. This shows that lower temperatures favour the production of alcohols which is facilitated by the hydrogenation of the carbonyl C=O bond and the suppression of esterification reaction. Consequently, as reaction temperature increases hydrogenation of carboxylic acids into esters and alkanes respectively can be further enhanced, thereby decreased selectivity to the alcohol will be obtained.⁴⁵ Though hydrogenation by the cleavage of C-O bond is facilitated at high temperatures resulting to higher conversion of carboxylic acids, the selectivity of C₁-C₄ alkanes and other gases was found to be $\leq 1\%$ which suggests that esterification was favoured via a reaction of produced alcohols and

unreacted carboxylic acids to produce esters. It was also observed that the solubility of acids in hexane solvent becomes stronger with decreasing polarity of the carboxylic acid as a result of non-polar interaction between them, which improves the hydrogenation of acids.⁴⁶

At 145 °C, 53% of acetic acid was converted into ethanol (52% selectivity) and ethyl acetate (48% selectivity) as the major products. The significant production of ethylacetate even at low temperature may be attributed to stronger adsorption of formed ethanol on the catalyst surface. Even at 200 °C, the selectivity to liquid products was $\geq 99\%$ which suggests that 4% Pt/TiO₂ does not favour further hydrogenation and decarboxylation reactions. The other trace products were thought to be gases as evident from product mass balance which was reported in earlier studies, such as ethane, methane and CO₂.^{18,36}

Table 7. Product distribution in hydrogenation of carboxylic acids over 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂ at 2 h

Temperature (°C)	Acid	4%Pt/TiO ₂			4%Pt-4%Re/TiO ₂		
		Conversion	S _{ALCOHOL}	S _{ESTER}	Conversion	S _{ALCOHOL}	S _{ESTER}
145	Acetic	53	52	48	54	70	30
	Propanoic	46.5	73.4	26.6	47	73.5	26.5
	Butanoic	48.2	98.5	1.5	60	98	2
165	Acetic	90	48	52	100	67.5	22.5
	Propanoic	86	61.6	38.4	97	72.9	27.1
	Butanoic	66.2	91.4	8.6	83	96.1	3.9
185	Acetic	98	46	54	100	69	31
	Propanoic	94	57.3	42.7	100	74.9	25.1
	Butanoic	88.2	80.3	19.7	100	95.7	4.3
200	Acetic	100	44	56	100	73	27

	Propanoic	100	44.9	55.1	100	76.4	23.6
	Butanoic	90.1	76.6	23.4	100	94.3	5.7

The conversion of propanoic acid at 145 °C was found to be 46.5%, and two liquid products were mainly observed under all temperatures: propanol (73% selectivity) and propyl propionate (27% selectivity). An increase in temperature from 145 – 165 °C significantly increased the conversion to 90% while alcohol selectivity decreased to 62%. Conversely, the selectivity to propyl propionate increased to 39% with increased temperature. Further increase in temperature to 200 °C shows that temperature has a profound effect on product formation which was evident in the decreased selectivity of propanol from 73 to 45 % and increased selectivity to propyl propionate from 27 to 55%. The resulting gaseous products from mass balance were insignificant and neglected as traces ($\leq 1\%$).

The hydrogenation of butanoic acid mainly resulted in butanol and butyl butyrate as primary products. As reaction temperature increases from 145 to 200 °C, butanoic acid conversion increased from 48.2 to 90.1%. Under these conditions, butanoic acid was highly selective to butanol with selectivity between 77 and 99%. The observed slower conversion of butanoic acid was mainly influenced by the hydrogenation pathway to butanol in comparison with acetic and propanoic acids, where conversion of the acids were via two pathways being mainly influenced by the esterification reaction.

The hydrogenation of carboxylic acids was carried out using 4%Pt-4%Re/TiO₂ under the same conditions as shown in Table 7. The reactions reached completion at 185 °C in all cases at 2 h. Even though the products remain the same as that of 4%Pt/TiO₂ for C₂-C₄ carboxylic acids, the addition of Re promoted the catalytic activity and alcohol selectivity over ester in all cases. A lack of a clear trend between the alcohol selectivity and Re content over Pt-Re/TiO₂ catalysts was reported by Manyar et al.¹³ in the hydrogenation of stearic acid. Elsewhere, Pritchard et al.²⁴

acknowledged that while increasing the Re content in Pt-Re/TiO₂ increases the conversion of methyl esters, the selectivity towards alcohol was not clear. The effect of Re in Pt-Re/TiO₂ catalysts was probed using the hydrogenation of acetic acid in section 3.7 of this study.

While acetic acid was completely converted at 165 °C, the selectivity to ethanol is 67.5% and selectivity to ethyl acetate is 32.5% for Pt-Re/TiO₂. The selectivity of ethanol linearly increased to 73% with an increase in temperature to 200 °C. It has been observed that Pt-Re/TiO₂ converts fatty acids into alkanes via alcohol;^{5,13} however, for short chain carboxylic acids such as acetic acid, the resulting synergy of Pt-Re on TiO₂ suppresses the dehydration-hydrogenation of ethanol into ethane, which, in turn, minimizes the interaction of oxygen atom in ethanol by enhancing desorption.

The catalyst performance for the hydrogenation of propanoic acid clearly shows that, at 185 °C, complete conversion was achieved, with a dominant selectivity of 74.9% towards propanol. At 200 °C, propyl propionate splits up into propanol and propanoic acid, which improves propanol selectivity to 76.4%.

In comparison with acetic and propanoic acids, hydrogenation of butanoic acid over 4%Pt-4%Re/TiO₂ showed improved catalyst activity in terms of butanol selectivity. Butanol selectivity was 98% at 145 °C, decreasing by only 3.7% as temperature increased to 200 °C. Similar results to our findings for the hydrogenation of butanoic acid was reported elsewhere for reaction at 265 °C over Ru/Ru-Sn/ZnO and 25 bar of hydrogen, which confirms that promotion of Pt/TiO₂ with Re can be used to achieve high alcohol selectivities under milder reaction conditions.⁴⁷ The observed increase in production of butanol over ethanol and propanol at higher temperatures could be associated with the increasing carbon number of the alkyl chain of alcohol which increases its thermal stability. This study shows that liquid phase hydrogenation of carboxylic acid (C₂-C₄) can

be achieved with significant selectivity towards alcohols ($\geq 70\%$) under reaction conditions reported for aqueous phase study.^{45,47}

3.5. Effect of time on the hydrogenation of C₂-C₄ carboxylic acids over 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂. The effect of reaction time on conversion and product selectivity was investigated on the hydrogenation of C₂-C₄ carboxylic acids using 4%Pt/TiO₂ at 185 °C and the results are shown in Table 8. Under these conditions, alcohols and esters were observed as the primary products and 100 % conversion was achieved in 3 h in all cases. It was also evident that de-esterification reaction occurred after the complete conversion of short chain carboxylic acids which gave rise to increased alcohol selectivity. The ester hydrolyses by splitting up into alcohol and acid as a result of equilibrium. It was also observed that further dehydration-hydrogenation reactions of alcohol to yield alkane products did not occur. With 4%Pt-4%Re/TiO₂ catalyst, the respective selectivity toward alcohol production increases from 59 to 75% (acetic acid), 67 to 78% (propanoic acid) and 95 to 98% (butanoic acid) as the reaction increases from 1 to 4 h. It is clear that as the molecular weight of the carboxylic acid increases the selectivity towards alcohol production increases, in this case butanoic > propanoic > acetic acid. However, with 4%Pt/TiO₂ catalyst for acetic acid the selectivity towards ethanol decreased as the reaction time increased from 1 to 2 h and increased as the reaction increased from 2 to 4 h. A similar observation can be noted for butanol selectivity with butanoic acid, except for propanoic acid in which propanol selectivity dropped as the reaction increased from 1 to 3 h and thereafter increased as the reaction time increased from 3 to 4 h. Overall, the alcohol selectivity decreases and subsequently increases as the reaction time increases from 1 to 4 h.

The hydrogenation of acetic acid required 1 h to achieve 89.6 % conversion over 4%Pt/TiO₂. The production of ethanol diminished between 1 to 2 h and began to increase afterwards until 4 h.

Further hydrogenation of ethanol after complete conversion of acetic acid did not occur even after 4 h which is likely dictated by the binding strength of oxygen metal bond.⁴⁸ In addition, the availability of oxygen defect sites (Ti^{3+}) on titania support provides a strong interaction with oxygen atom in ethanol, and prevents the ethoxy group from further reaction with adsorbed hydrogen.

During the hydrogenation of propionic acid, the selectivity of propanol decreased from 73% to 52% while propyl propionate increased from 27% to 48% over a period of 1 h to 3 h. After the complete conversion of propanoic acid, the selectivity of propanol slightly improved to within 2% as a result of hydrolysis of propyl propionate.

Butanoic acid conversion increases from 55% to 100% in the range of 1-4 h. At the beginning of the reaction, the selectivity of butanol was 87.5% and butyl butyrate was 12.5%. However, as the reaction proceeds from 1-2 h, the selectivity of butanol gradually decreased to 80.4% and subsequently increased to 84.2% from 2-4 h.

Table 8. Product distribution in hydrogenation of carboxylic acids over 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂ at 185 °C.

Time (h)	Acid	4%Pt/TiO ₂			4%Pt-4%Re/TiO ₂		
		Conversion	S _{ALCOHOL}	S _{ESTER}	Conversion	S _{ALCOHOL}	S _{ESTER}
1	Acetic	89.6	53	47	94	59	41
	Propanoic	51.4	73.1	26.9	81	67	33
	Butanoic	55.3	87.5	12.5	79	95	5
2	Acetic	98	46	54	100	64	36
	Propanoic	94	57.3	42.7	100	75	25
	Butanoic	88.2	80.3	19.7	100	94	6
3	Acetic	99	64	36	100	72	28

	Propanoic	100	52.4	47.6	100	76	24
	Butanoic	100	82.7	17.3	100	96	4
4	Acetic	99	67	33	100	75	25
	Propanoic	100	53.8	46.2	100	78	22
	Butanoic	100	84.2	15.8	100	98	2

The effect of reaction time on the hydrogenation of C₂-C₄ carboxylic acids was investigated using 4%Pt-4%Re/TiO₂ as shown in Table 8. Interestingly, the reaction reached completion after 2 h for C₂-C₄ carboxylic acids which confirms improved catalyst performance when Re acts as a promoter.^{5,24} It was observed that the selectivity towards alcohol increases with time. Butanoic acid showed significant selectivity towards butanol with $\leq 5\%$ selectivity to butyl butyrate under the different reaction times. In a mixture of biobutanol as a fuel, butyl butyrate holds a strong potential as a sustainable biofuel additive which enhances the ignition properties of the blended fuel.^{49,50} Thus, the utilization of butyl butyrate makes the hydrogenation of butanoic acid more attractive towards the upgrading process. Overall, the catalyst activity observed over 4%Pt/TiO₂ and 4%Pt-4%Re/TiO₂ could be attributed to sustained oxygen vacancy sites over time, and moderate acidity from the TiO₂ support to allow hydrogenation to occur.³⁶

3.6. Catalyst Reusability Test. The reusability of 4%Pt/TiO₂ catalyst was investigated by recovering the fresh and 1st reused catalysts at the end of hydrogenation of acetic acid. The recovered catalysts were regenerated for reuse by washing with acetone and drying at 120 °C for 2 h, then subsequent pre-reduction under hydrogen atmosphere for 65 mins. The reusability of the 4%Pt/TiO₂ as function of time is shown in Figure 5. The acetic acid conversion and ethanol selectivity followed a similar trend for the fresh, first and second reuse tests carried out. The conversion of acetic acid decreased from fresh to second reuse, likewise, the selectivity towards

ethanol production. This slight drop in acetic acid conversion and ethanol selectivity can be attributed to the reduced strength in active sites after successive reaction and regeneration. It can be observed that this drop is very narrow.

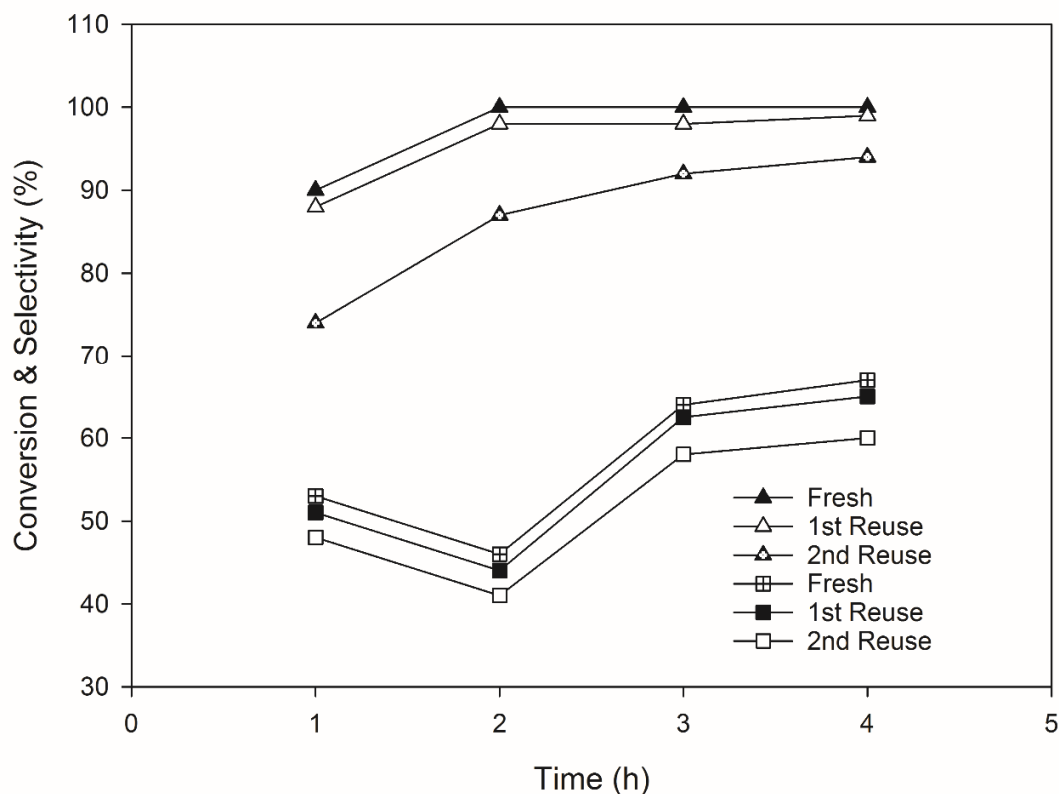


Figure 5. Reusability of monometallic 4%Pt/TiO₂ catalyst is shown by the hydrogenation activity in terms of acetic acid conversion and ethanol selectivity with respect to time. Triangle – Conversion of acetic acid; Square – Selectivity of ethanol (Reaction conditions: catalyst 0.3 g, initial concentration 0.2 M, temperature 185 °C, pressure 40 bar, hexane 50 ml).

In all cases, the ethanol selectivity decreased as the reaction time increased from 1 to 2 h and, thereafter, increased as the reaction time increased from 2 to 4 h. The fresh and the two cycles of reuse followed the same pattern with little decrease in the catalyst performance for both conversion

and selectivity between the fresh and the first reuse test for 4 h experiment. However, further drop in the catalyst performance was observed for second reuse test for 4 h experiment compared to the fresh catalyst, which suggests minimal 4%Pt/TiO₂ catalyst deactivation attributed to material deposit leading to decreased strength of the active sites.

3.7. Effect of Rhenium (Re) loading in Hydrogenation of carboxylic acids. Figure 6 shows the conversion and the respective selectivity of ethanol and ethylacetate for the hydrogenation of acetic acid as a function of the ratio of Pt to Re on a TiO₂ support. The conversion of acetic acid increases as the loading of Re increases from 0 to 4% when the loading of Pt on TiO₂ was held constant (4%). It was reported that higher metal loadings above 4% may cause agglomeration which could be detrimental to catalyst activity.⁵¹ While the selectivity of ethanol increases as the loading of Re on the 4%Pt/TiO₂ increases from 0 to 4%, the selectivity of ethylacetate decreases in a similar manner. This further reinforces the notion that the presence of Re magnifies the hydrogenation reaction towards ethanol production while at the same time suppressing esterification and ethylacetate formation. This observation is true for the C₂-C₄ carboxylic acids investigated (Tables 7 and 8).

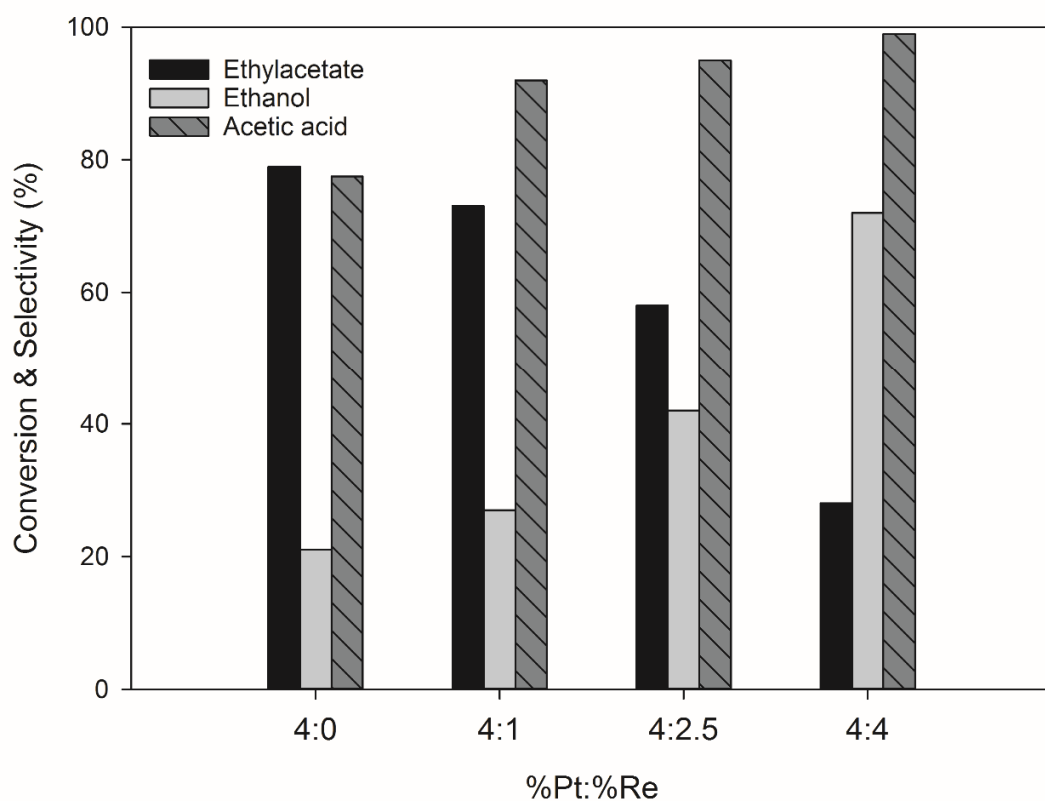


Figure 6. Evaluation of Pt-Re (x:y)/TiO₂ catalysts in the hydrogenation of acetic acid. (Reaction conditions: catalyst 0.3g, initial concentration 0.2 M, reaction time 4h, pressure 40 bar, temperature 200 °C).

Specifically, as the Re loaded on the 4%Pt/TiO₂ increased from 0 to 4%, the ethanol selectivity increased from around 20 to 74% representing an approximately 73% increase by adding 4% Re to 4% Pt/TiO₂. A similar effect on acetic acid conversion gives a 22% increase and for ethylacetate selectivity there is a 65% decrease. Notably, when 4%Re/TiO₂ was tested alone in the absence of Pt, low acetic acid conversion of about 40% and low ethylacetate selectivity of about 3% were observed (Figure 2). This reaffirms that the presence of Pt exerts much influence on the catalyst

activity as observed by increased conversion (H_2 dissociation), and the promotion of the esterification reaction leading to ethylacetate formation (Figures 2,6 and Tables 7,8).

4. CONCLUSIONS

The batch catalytic hydrogenation of model carboxylic acids ($\text{C}_2\text{-C}_4$) commonly found in bio-oils was carried out using supported Pt and Pt-Re on TiO_2 catalysts prepared via impregnation, under optimised reaction conditions. Catalyst screening showed that prepared 4%Pt/ TiO_2 and 4%Pt-4%Re/ TiO_2 catalysts outperformed commercial catalysts for acetic acid hydrogenation, and were found to favour ethylacetate and ethanol respectively. The Taguchi optimization method revealed 200 °C, 40 bar H_2 , 0.4 g catalyst loading, 1000 min^{-1} and 4 h were the optimum conditions for acetic acid conversion while 160 °C, 40 bar H_2 , 0.4 g catalyst loading, 1000 min^{-1} and 4 h were the optimum conditions for ethanol yield. Hydrogenation of butanoic acid was found to be more selective towards alcohol than lower molecular weight acids. In all cases, alcohol selectivity was observed to decrease with increased temperature. While 4%Pt/ TiO_2 mostly favoured ester production, 4%Pt-4%Re/ TiO_2 favours alcohol production. The effect of Re addition to 4%Pt/ TiO_2 was investigated using hydrogenation of acetic acid and showed that acetic acid conversion and ethanol yield were linearly improved on increasing Re from 1 to 4wt%.

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SUPPORTING INFORMATION

Effect of stirring speed on initial rate, conversion and external mass transfer (Figure S1).

XRD pattern for fresh 4% Pt/TiO₂ catalyst (Figure S2)

EDX mapping image of 4% Pt/TiO₂ catalyst (Figure S3).

Surface area and pore size of platinum catalysts by BET and BJH models (Table S1)

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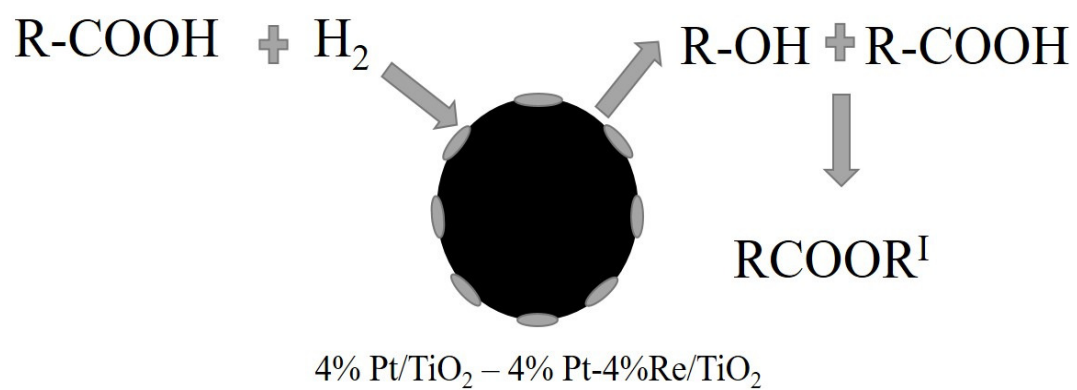


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